Investigating the Photooxidation of $CHBr_3$: Matrix-Isolation, Gas-Phase, and DFT Study

Michelle T. Custodio Castro*, Rosana M. Romano

Department of Chemistry, Faculty of Exact Sciences, Center for Inorganic Chemistry "Dr. Pedro J. Aymonino" (CEQUINOR), National University of La Plata (UNLP), CCT-CONICET La Plata, associated with CIC-PBA, La Plata, B1900, Argentina.

mcustodiocastro@quimica.unlp.edu.ar

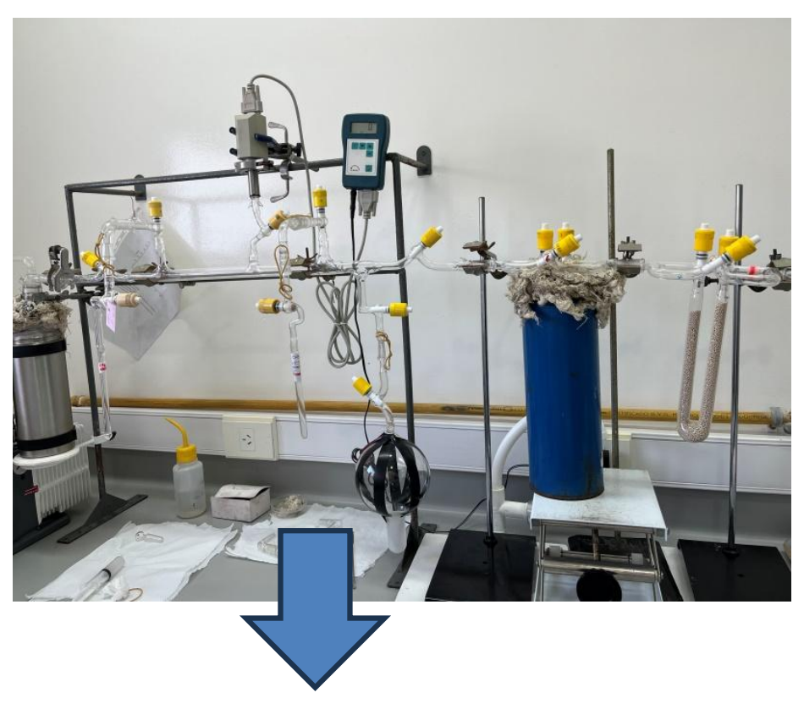
INTRODUCTION & AIM

Bromoform ($CHBr_3$) is a very short-lived substance (VSLS) in the troposphere, emitted mainly from natural sources (e.g., phytoplankton and macroalgae).[1] It contributes to the formation of reactive bromine species that participate in ozone depletion.[2]

Here, we investigate the **UV-vis photooxidation of $CHBr_3$** using matrix-isolation FTIR spectroscopy combined with DFT calculations, aiming to elucidate the underlying photoreaction mechanism.

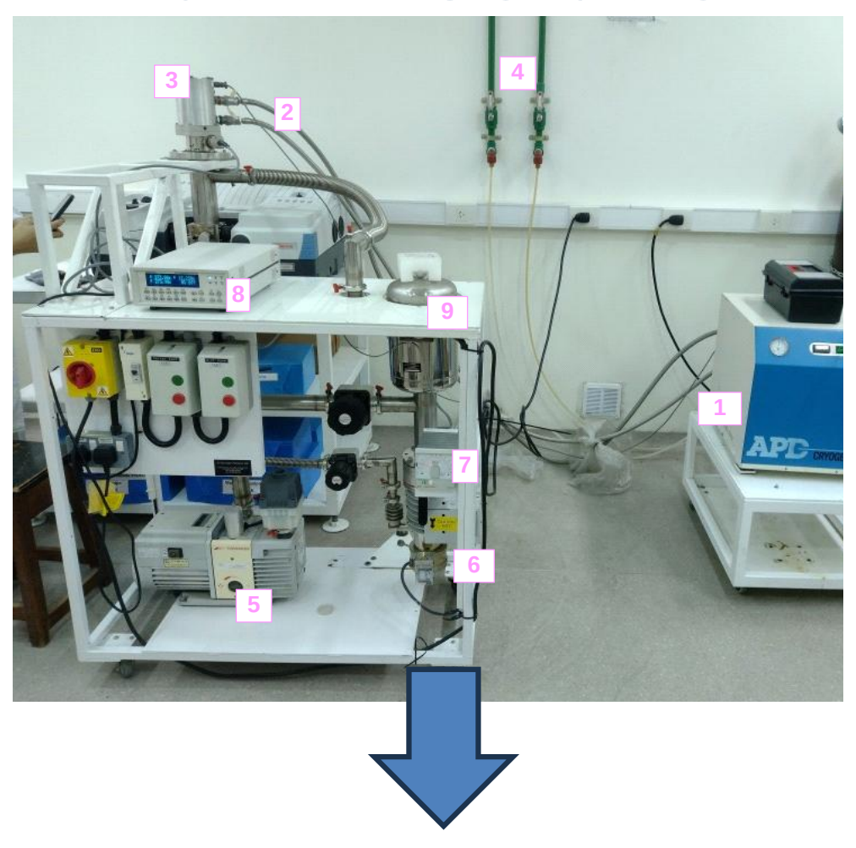
METHOD

Gas mixture preparation



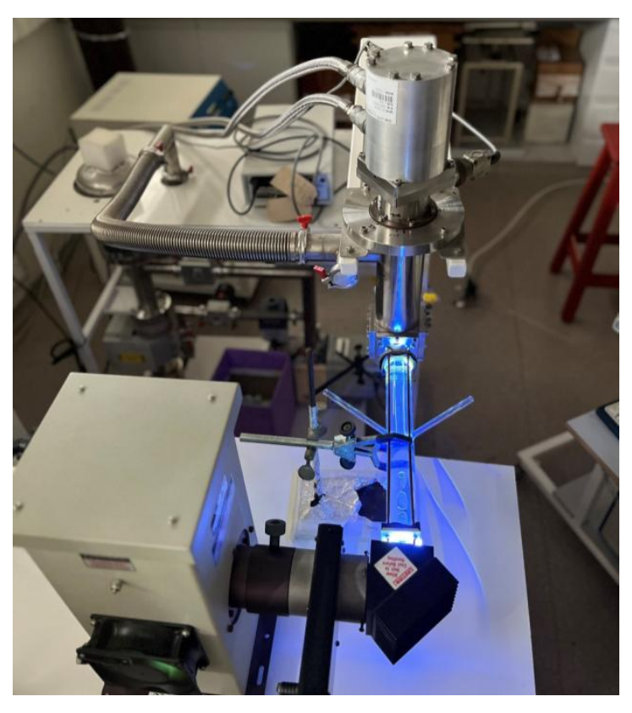
$CHBr_3$:O_2:Ar mixtures (1:1:400 and 1:20:400) prepared using standard manometric techniques.

Matrix isolation

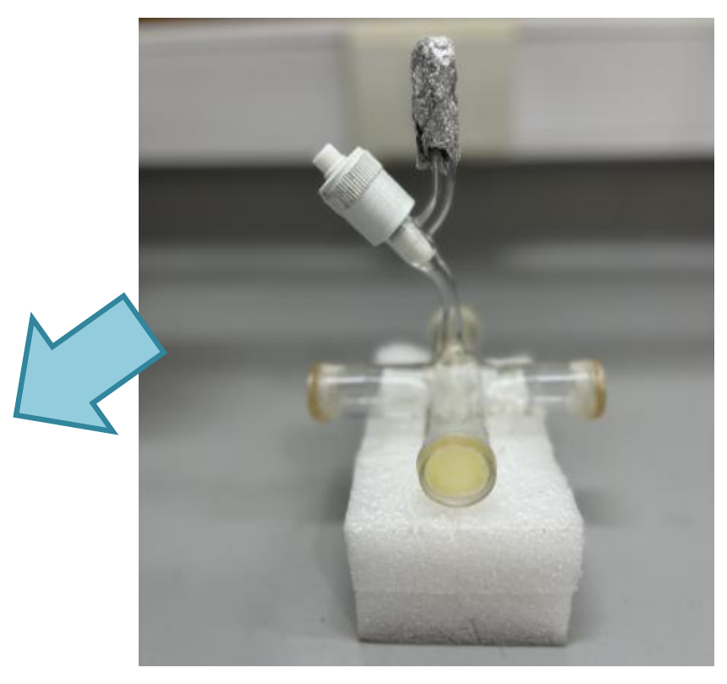


The mixtures were deposited on a CsI window cooled at **10 K** using a pulse-deposition technique.

UV-Vis irradiation



Gas phase

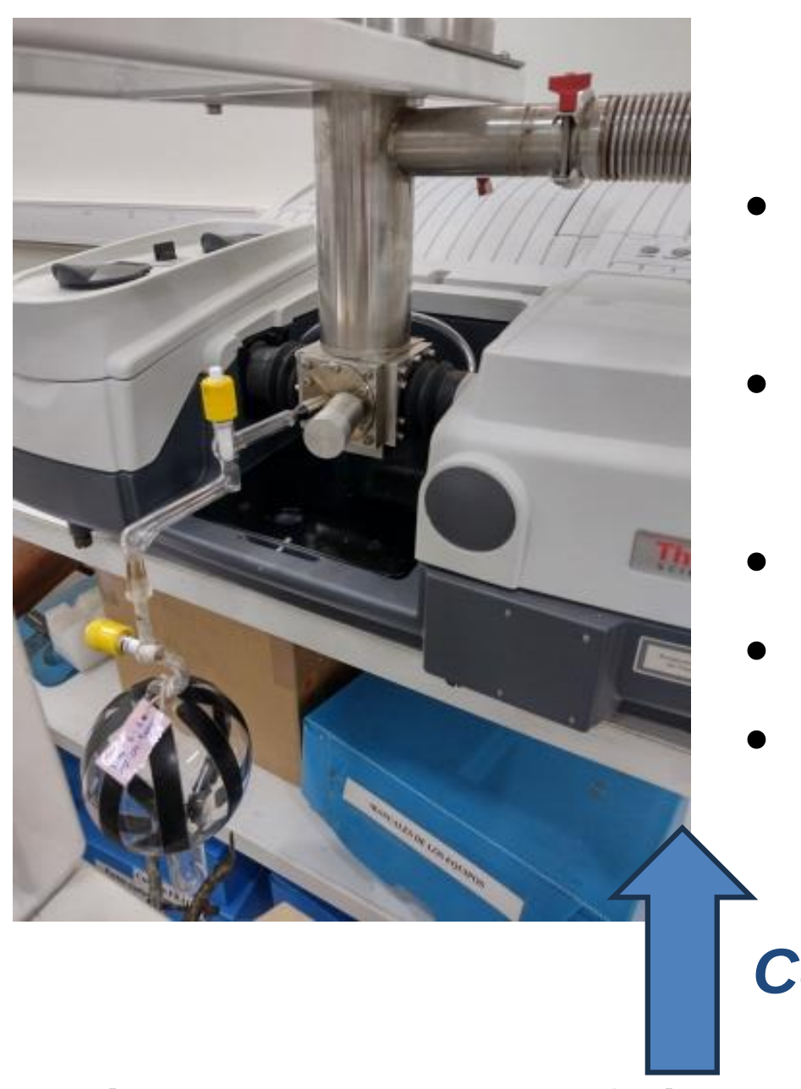


Room temperature

UV-vis irradiation using a Xe(Hg) arc lamp (800 W). Selected spectral intervals were used:

- 280–320 nm (UV-B),
- 350–450 nm (UV-A),
- 400–800 nm (visible),
- and 200–800 nm (full range).

FTIR



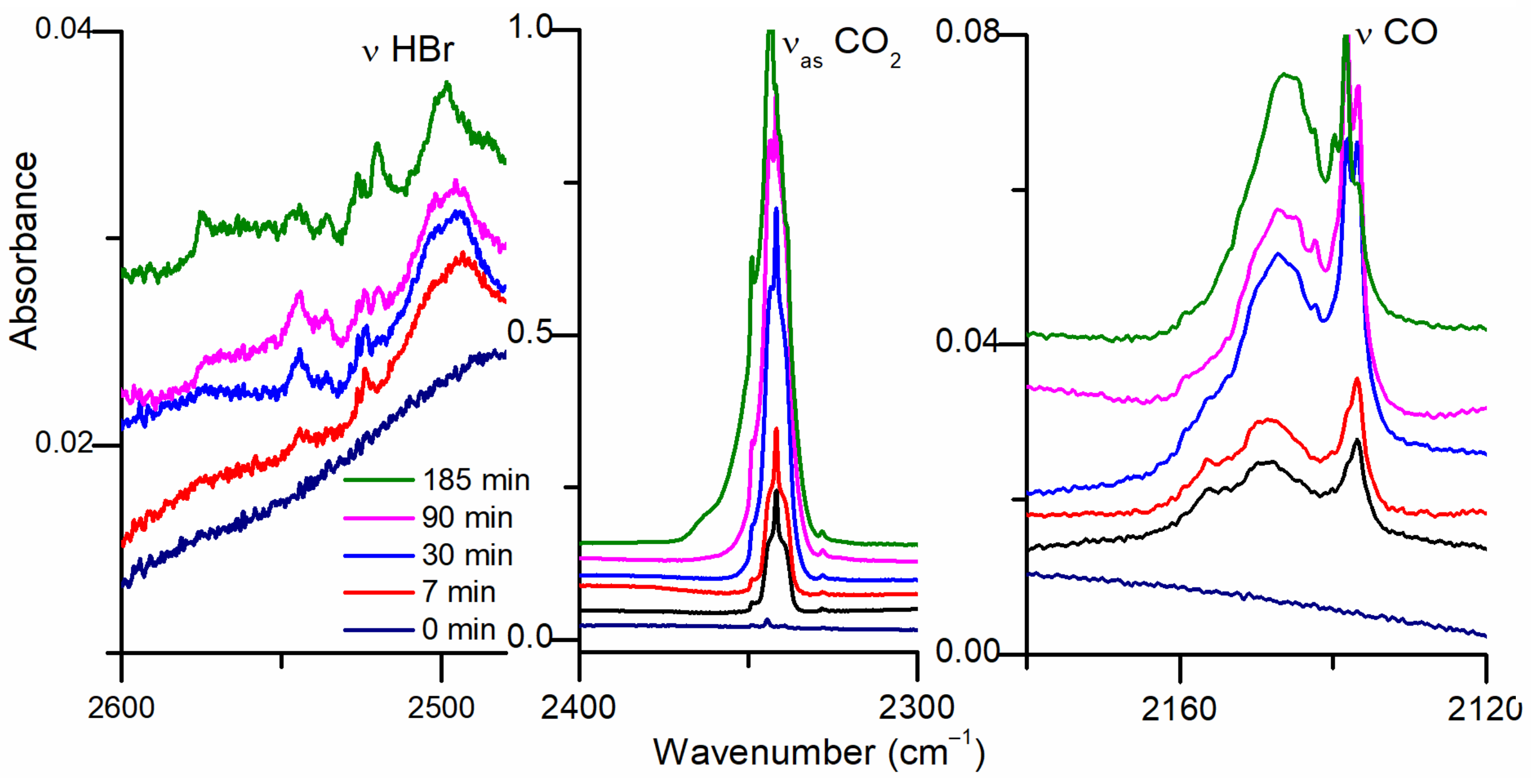
- Thermo Nicolet 6700 spectrometer
- Deuterated Triglycine Sulfate (DTGS) detector
- KBr beamsplitter
- Spectra acquisition from 4000 to 400 cm-1

Comparison

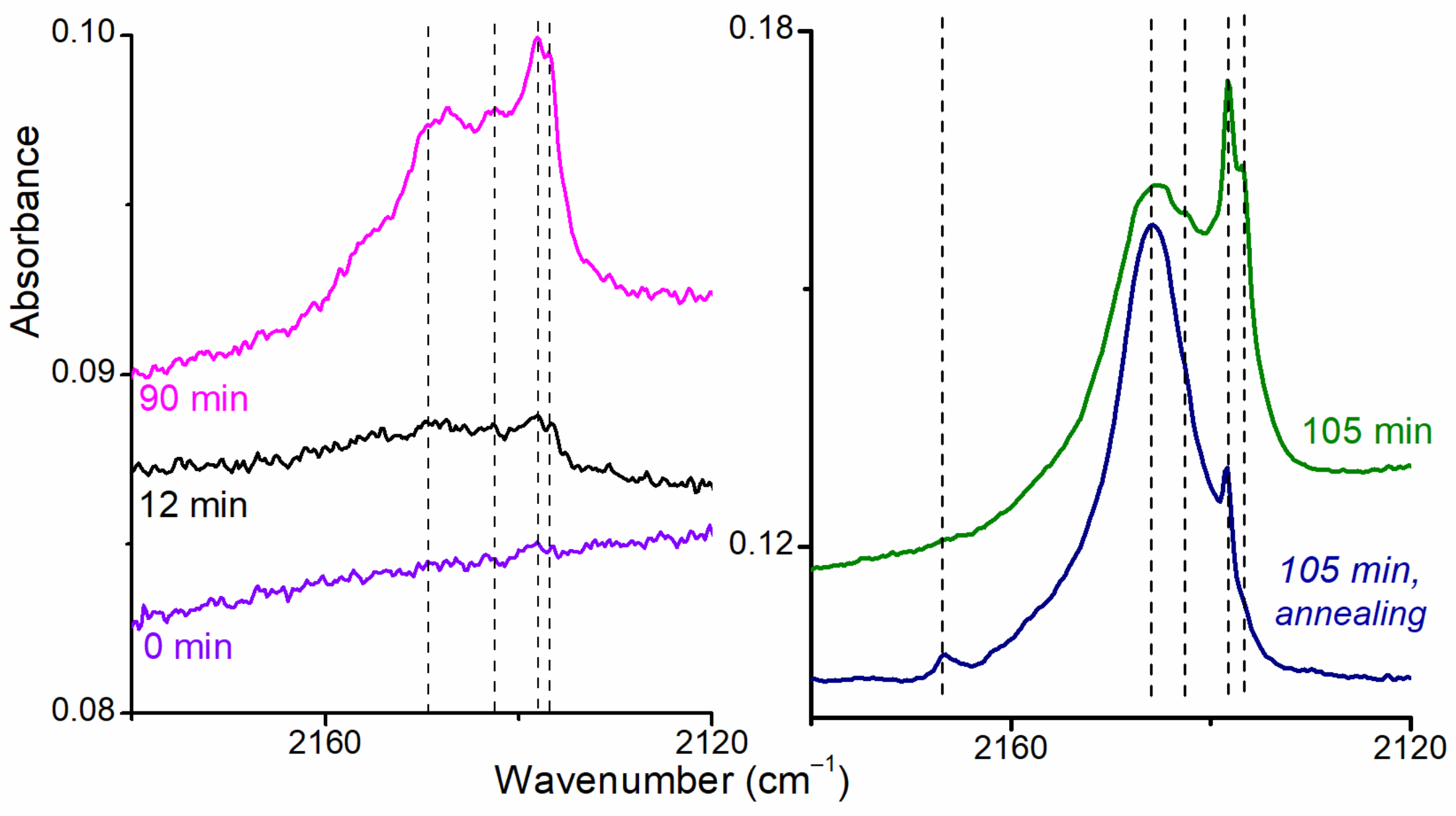
- The structures of the possible intermolecular complexes formed among the photoproducts were theoretically simulated using the **B3LYP-D3/6-311++G(d,p)** approximation

RESULTS & DISCUSSION

(A) INITIAL MATRIX SPECTRA. $CHBr_3$:O_2:Ar matrices (1:1:400 and 1:20:400) show only $CHBr_3$ bands. Under analogous conditions in $CHBr_3$:Ar matrices (i.e., in the absence of O_2), $CHBr_3$ dimeric and trimeric species have been previously characterized by our group.[3]



FTIR spectra of $CHBr_3$:O_2:Ar (1:20:400) matrices (0.5 cm−1 resolution) in selected regions. Left: ν(HBr), center: $\nu_{as}(CO_2)$ and right: ν(CO). Spectra recorded after increasing UV irradiation times (0-185 min).



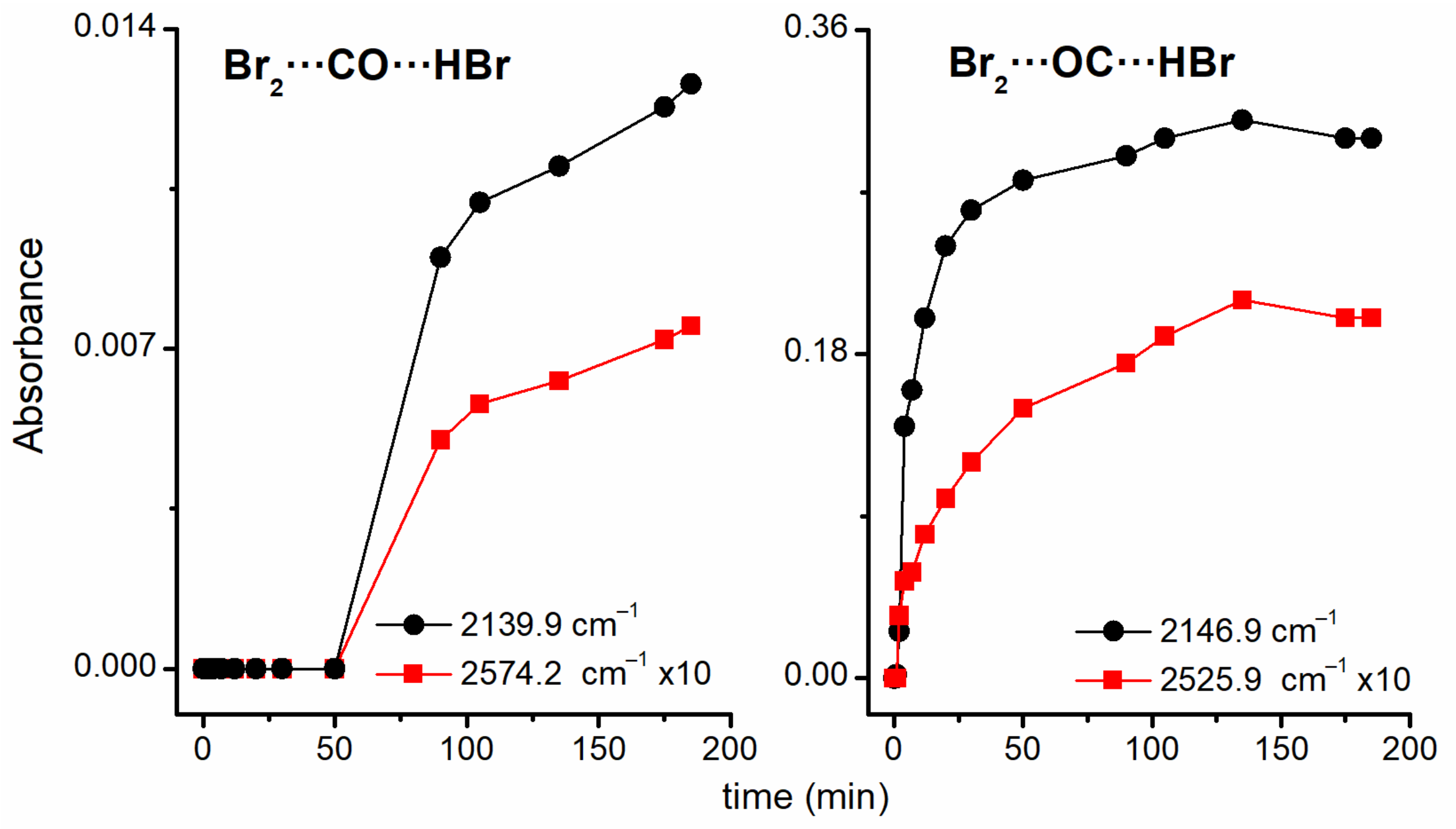
FTIR spectra in the CO stretching region of $CHBr_3$:O_2:Ar (1:20:400) matrices (0.5 cm−1 resolution).
Left: after deposition and after 12 and 90 min of UV irradiation (200≤ λ ≤ 800 nm).
Right: after 105 min of UV irradiation and after annealing

(B) PHOTOCHEMICAL EVOLUTION

After irradiation with broadband UV-vis light (**200≤ λ ≤ 800 nm**) and using irradiation with **350≤ λ ≤ 450 nm**, new bands appeared in the absorption region of **HBr, CO_2 and CO.**

Bands assigned to HBr, CO_2, and CO exhibit **correlated growth kinetics** and increase in intensity upon **annealing**.

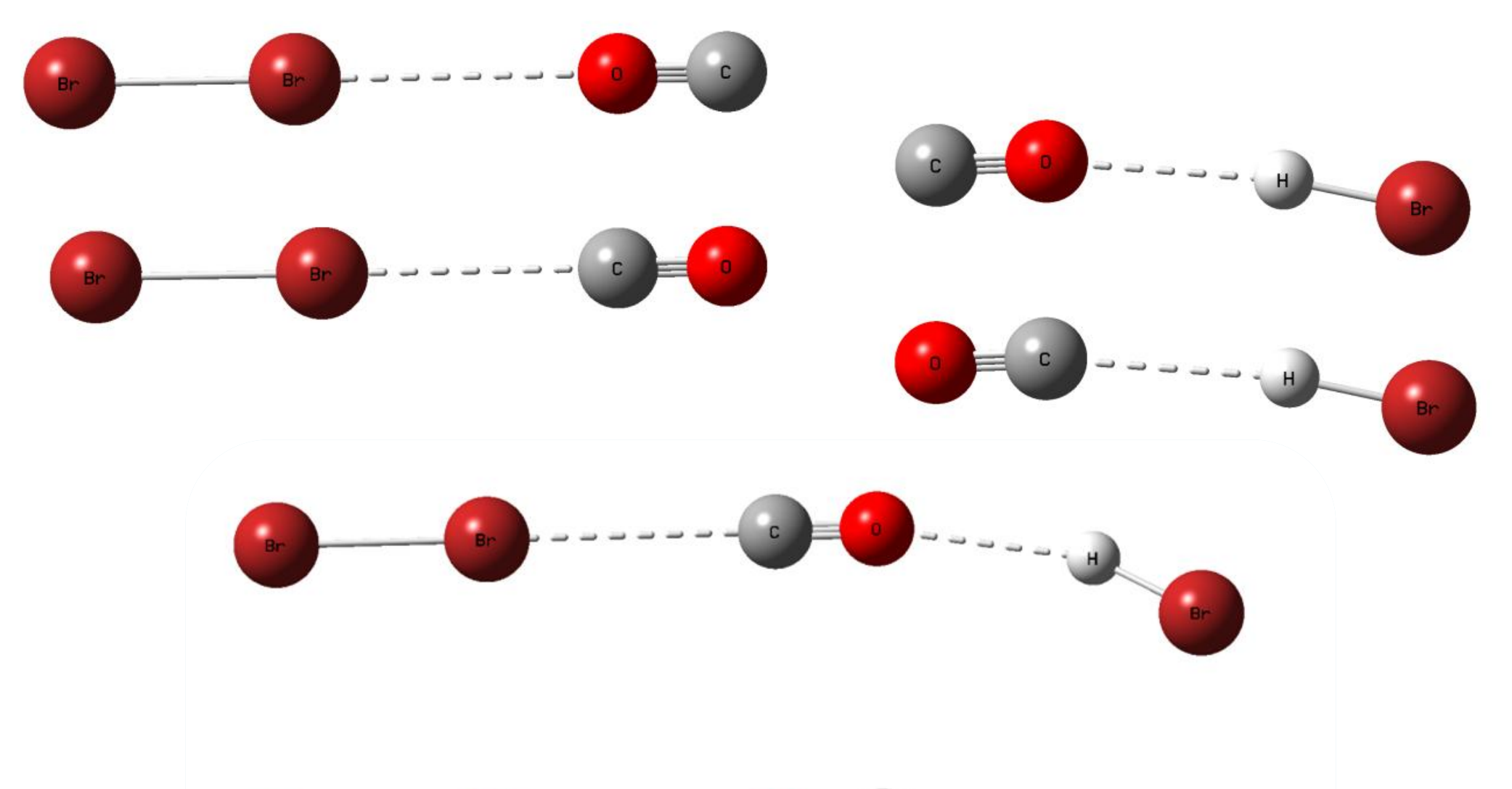
Gas-phase studies performed in a home-built cell with simultaneous irradiation and FTIR detection ***HBr, CO_2 and CO*** were detected as photoproducts.



Plots of the intensities of the bands in the FTIR spectra of the $CHBr_3$:O_2:Ar (1:20:400) at about 10 K vs irradiation times with broad-band UV-vis irradiation (200≤ λ ≤ 800 nm).

(C) ASSIGNMENT AND THEORETICAL SUPPORT

Theoretical IR spectra of all energy-minimized structures were compared with the experimental spectra



Optimized molecular structures of complex between Br_2, CO and HBr. Geometries were calculated at the B3LYP-D3/6–311++G(d,p) level of theory

Table 1. Experimental wavenumbers observed after the irradiation of $CHBr_3$:O_2 mixtures in an Ar matrix, and comparison with the calculated values for the proposed photoproducts.

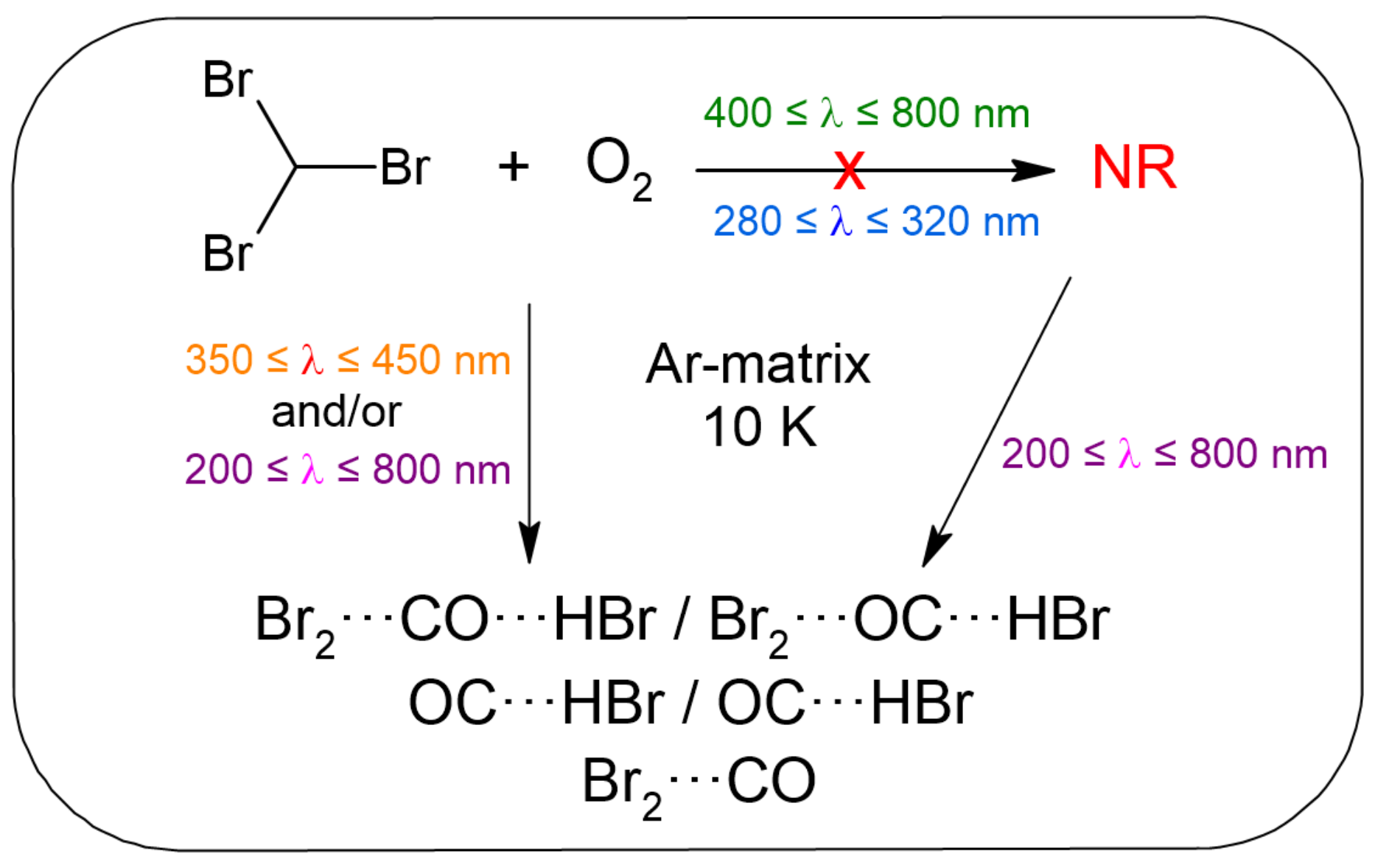
	Ar-matrix		B3LYP-D3/ 6-311G++(d.p)	Ref.
	ν (cm−1)	$\Delta\nu_{exp}$ (cm−1)	$\Delta\nu_{teor}$ (cm−1)	
Br_2···CO···HBr	2574.2	17.7[a]	16.3	
	2142.2/2139.9	1.7	3.6	
Br_2···OC···HBr	2525.9	–30.5[a]	–39.6	
	2146.9	8.7	10.9	
OC···HBr	2520.4	–36.1[a]	–42.2	2520[b] 2520.1[c]
	2152.8	14	16.6	2152[b] 2152.4[c]
CO···HBr	2136.7	–1.5	–9.2	
Br_2···CO	2144.2	5.9	13.2	2144.3[d]

a) Picone, A.L., Universidad Nacional de La Plata (**2008**). b) Lasson, E. et. al. Acta Chem. Scand. 51, (**1997**) 1–7. c) Andrews, L. et al., J. Chem. Phys. 78 (**1983**) 6347–6352. d) Romano, R.M. et al, Inorg. Chem. 44 (**2005**) 3241–3248.

CONCLUSIONS

Under UV–vis irradiation (200–800 nm and 350–450 nm), the formation of **intermolecular complexes involving HBr, CO and Br_2** was evidenced by matrix-isolation FTIR and supported by theoretical calculations, providing molecular-level insight into the photochemical processes.

Proposed photochemical mechanism in Ar matrices at 10 K.



REFERENCES/ACKNOWLEDGMENT

(1) J. Villamayor et al. *Nat. Clim. Chang.* 13 (**2023**) 554–560.
(2) L. Tinel et al. *Elem. Sci. Anthr.* 11:1 (**2023**) 00032.
(3) Custodio Castro et al. J. Mol. Struct. 1366 (**2026**) 146021.

The authors acknowledge the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) (PIP 0352 and PUE-2017-22920170100053), the Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT) (PICT-2020-03746), and the Universidad Nacional de La Plata (UNLP-X971) for providing financial support.